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(54) Title: SKEKETAL ISOMERIZATION OF FATTY ACIDS

(57) **Abstract:** The present invention relates to a process for the skeletal isomerization of unsaturated linear fatty acids to branched fatty acids which comprises contacting said unsaturated linear fatty acids with at least one large pore zeolite catalyst wherein said at least one zeolite catalyst comprises a material having a three dimensional channel structure having a pore diameter of at least 6.0 Å. In another embodiment, the invention relates to a process for the skeletal isomerization and hydrogenation of unsaturated linear fatty acids to saturated branched fatty acids which comprises contacting said unsaturated linear fatty acids with at least one metal-zeolite catalyst.

SKELETAL ISOMERIZATION OF FATTY ACIDS

Field of the Invention

The present invention generally relates to a process for the isomerization of
5 unsaturated fatty acids with a catalyst to branched fatty acids.

Background of the Invention

Fatty acids are the building blocks for various compositions ranging from
lubricants, polymers, solvents, cosmetics and the like. Fatty acids are generally
10 obtained by hydrolysis of triglycerides of vegetable or animal origin. Naturally
occurring triglycerides are esters of glycerol and generally straight chain, even
numbered carboxylic acids, in size ranging from 10-24 carbon atoms. Most
common are fatty acids having 12, 14, 16 or 18 carbon atoms. The fatty acids
are either saturated or contain one or more unsaturated bonds.

15 Long, straight chain saturated fatty acids (C10:0 and higher) are solid at room
temperature, which makes them difficult to process in a number of applications.
Unsaturated long chain fatty acids, however, e.g. oleic acid are liquid at room
temperature, so are easy to process, but are unstable because of the existence
20 of double bond(s). Branched fatty acids mimic the properties of the straight chain
unsaturated fatty acids in many respects, but do not have the disadvantage of
being unstable. "Branched fatty acids" means fatty acids containing one or more
alkyl side groups which are attached to the carbon chain backbone at any
position. Therefore, branched fatty acids are for many applications more
25 desirable than straight chain fatty acids. Commercial branched acids are not,
however, naturally occurring materials.

Currently, branched fatty acids are obtained by isomerization (branching) of the
straight chain, unsaturated fatty acids having a corresponding chain length. For
30 example, branched C18:0 is prepared from straight C18:1, a C18 with one
unsaturated bond, (or also C18:2, a C18 with two unsaturated bonds). Various
routes are known for said isomerization or branching of fatty acids in the art.

In one process, for example, clay is used as a catalyst. This clay catalyzed isomerization suffers from two main disadvantages. First, a considerable amount of undesired side products containing oligomers, saturated straight chain fatty acids and intermediate dimers is formed. A second disadvantage is that the clay 5 catalyst cannot be reused.

U.S. Patent No. 5,856,539 discloses an isomerization process whereby a fatty acid feed comprising unsaturated fatty acids is contacted with a catalyst, characterized in that the catalyst comprises a material having a microporous 10 structure.

U.S. Patent No. 5,677,473 describes a process for preparing branched chain fatty acids or alkyl esters thereof which comprises subjecting unsaturated fatty acids having 10-25 carbon atoms or alkyl esters thereof to a skeletal 15 isomerization reaction in the presence of water or a lower alcohol using a zeolite as a catalyst. The zeolite has a linear pore structure of a size small enough to retard dimerization and large enough to allow diffusion of the branched fatty acids or alkyl esters thereof.

20 U.S. Patent No. 5,364,949 describes a process for the production of branched fatty acids and their esters which comprises reacting unsaturated fatty acids or esters thereof with aliphatic nonactivated olefins in the presence of layer silicates and active carbon.

25 However, all of these processes are plagued by low yield and/or a high rate of undesirable byproduct formation. Accordingly, there is a need for a new process that overcomes these disadvantages, i.e. a process for the preparation of branched fatty acids from straight chain unsaturated fatty acid feedstocks with a high conversion rate, an increased selectivity towards branched monomeric 30 isomers and which employs a reusable catalyst.

Summary of the Invention

The present invention generally relates to a process for the skeletal isomerization of unsaturated linear fatty acids to branched fatty acids which

5 comprises contacting said unsaturated linear fatty acids with at least one large pore acidic catalyst having a three dimensional channel structure. In another embodiment, the invention relates to a process for the skeletal isomerization and hydrogenation of unsaturated linear fatty acids to saturated branched fatty acids which comprises contacting said unsaturated linear fatty acids with at least one

10 acidic catalyst loaded with at least one metal capable of hydrogenating unsaturated chemical bonds in the presence of hydrogen or a hydrogen source. The invention also relates to various softener compositions comprising actives prepared from the branched fatty acids of the present invention.

15 Detailed Description of the Present Invention

The present invention generally relates to a process for the skeletal isomerization of unsaturated linear fatty acids to branched fatty acids which comprises contacting said unsaturated linear fatty acids with at least one large

20 pore acidic catalyst having a three dimensional channel structure. The present process advantageously converts fatty acid feedstock into a mixture that is rich in branched fatty acids and low in oligomers. While the reaction products of the present process will generally comprise both saturated as well as unsaturated branched fatty acids, both are thus included in the invention, there is high

25 selectivity towards the formation of branched fatty acids. Optionally, the unsaturated branched fatty acids may be hydrogenated in any conventional way.

The acidic catalyst of this embodiment is characterized in that it comprises a material having a three dimensional pore structure wherein at least one of the

30 channel structures has a pore size large enough to allow diffusion of the branched fatty acids and/or alkyl esters thereof. More particularly, at least one of the channel structures has a pore size large enough for the fatty acid to enter the

pore and access the internal active sites. Typically, this pore size is at least about 5.5 Å, preferably at least 6.0 Å. Catalysts of this type having a three-dimensional channel structure have higher activity and are not as readily deactivated by pore mouth blockages compared to catalysts having one and/or

5 two dimensional channel structures.

Various acidic catalysts having the required three dimensional pore structure and size are known to the skilled artisan. Examples of acidic catalysts employable in the claimed process include but are not limited to zeolites, acidic clays,

10 molecular sieves and the like.

Zeolites are crystalline aluminosilicates generally represented by the formula



15 where M is a metal cation of groups IA including Hydrogen or IIA and n is the valency of this metal. Zeolites consist of a network of SiO_4 and AlO_4 tetrahedra linked together via shared oxygen atoms. Aluminum has a 3^+ valency resulting in an excess negative charge on the AlO_4 tetrahedra, which can be compensated by cations such as H^+ . When M is hydrogen the materials are Bronsted acidic, when M is for example Cs the materials are basic. Upon heating, Bronsted acidic hydroxyls condense creating coordinately unsaturated Al, which acts as a Lewis acid site. The acid strength, acid site density and Bronsted versus Lewis acidity are determined by the level of framework aluminum. The ratio of silica/alumina

20 can be varied for a given class of zeolites either by controlled calcination, with or without the presence of steam, optionally followed by extraction of the resulting extra framework aluminum or by chemical treatment employing for example ammonium hexafluorosilicate.

25

30 As zeolite frameworks are typically negatively charged, the charge balancing cations related to this invention include monovalent cations such as H^+ , Li^+ and the like, divalent cations such as Mg^{2+} , Zn^{2+} and the like and trivalent cations

such as Ln^{3+} , Y^{3+} , Fe^{3+} , Cr^{3+} and the like. The framework composition of the three-dimensional zeolites may contain other elements in addition to Al and Si, such as, for example, P, Ti, Zr, Mn, and the like. Although any zeolite meeting the parameters of the present invention can be employed, faujasite Beta zeolite, 5 Y zeolite, Offeretite and the like are particularly well suited for the present process. The Si/Al ratio of the zeolites can vary depending on the particular zeolite employed provided that the skilled artisan understands that a ratio which is too low will result in more by-products and a ratio which is too high will lower the activity of the zeolite. In most cases the Si/Al ratio of the zeolites is at least 2, 10 up to at least 20 and higher. For example, the Si/Al ratio for Beta zeolite may be from about 25-75 while that for Y zeolite can be from 30 to about 80.

Zeolites employable in the present process comprise a three-dimensional pore structure wherein at least one channel structure has a pore size large enough to 15 allow diffusion of the branched fatty acids and/or alkyl esters thereof. In general, the larger the number of oxygen atoms in the ring opening, the larger the pore size of the zeolite. But this size is also determined by the structural shape of the ring. Zeolite materials having a three dimensional channel structure and a pore size of at least about 6.0 Å can generally be employed in the process of the 20 invention. Such pore structures having a pore size of at least about 6.0 Å generally comprise 10 and/or 12 membered rings, or even larger rings in their structures.

It is known that zeolites having a three dimensional channel structure can be 25 formed by zeolites having one dimensional channel with certain mineral acids such as nitric acid, hydrochloric acid and the like, and/or certain organocarboxylic acids such as acetic acid and oxylic acid and the like. Other methods for generating zeolites with a three dimensional channel structure are known to the skilled artisan.

30

The subject process contemplates both batch and fixed bed continuous processes which utilize the aforementioned zeolites.

Good selectivity and conversion can be obtained by the process of the present invention if at least part of the isomerization is performed at a temperature of between about 100° C and 350° C. In another embodiment, the process of the 5 invention is performed at a temperature of between about 230° C and 285° C. Since the conversion is also a function of the reaction/contact time, it is preferred that the fatty acid feedstock is contacted with the catalyst for a period of at least 30 minutes and reaction times of 1-16 hours are typical. An even longer period could be used if the process is operated at a lower temperature.

10

In general, the amount of catalyst employed in the process according to the invention is between 0.5 and 20% by weight, based on the total reaction mixture. In another embodiment the amount of catalyst used between 2.5 and 10% by weight. In still another embodiment the catalyst amounts are between 3 and 7% by weight.

For a continuous process the amount of catalyst used is preferably between 0.5 and 20% by weight of the space velocity of the feedstock. The space velocity is the amount of feed per hour per volume of catalyst. More specifically, with a 20 space velocity range of 0.01 to 100, we mean that the feed is passed through a catalyst at [(weight of feed per hour) /volume of catalyst] = 0.01 to 100. For example, at a space velocity of 1.0, the amount of feed in weight (g) per hour is equal to the volume of catalyst (ml). A space velocity of 0.01 means the feed is introduced at extremely slow flow rate to the reactor, i.e. 1/100 of the feed rate 25 with respect to space velocity of 1.0, while the catalyst volume inside the reactor remains the same.

Additionally, it has been found that by using the catalyst system according to this invention it is possible to reuse the catalyst. In some cases it may be desired to 30 add fresh catalyst while optionally removing a part of the spent catalyst, and in other cases regeneration of the catalyst may be desired. Regeneration can be effected by various methods known to the skilled artisan. For example,

regeneration can be accomplished by utilizing controlled oxidative regeneration and/or by washing with a solvent.

Typical feedstocks comprise unsaturated linear alkylcarboxylic acids, related
5 esters or mixtures thereof, optionally containing other organics. Since the present process is designed for isomerization or conversion of unsaturated fatty acids into branched fatty acids, it is beneficial if the fatty acid feed comprises of at least about 30% by weight of unsaturated fatty acids. In another embodiment, the feedstock comprises at least 50% by weight of unsaturated fatty acids. Any
10 unsaturated and/or polyunsaturated fatty acid, or mixtures thereof is suitable as a feedstock in accordance with the present invention. In one embodiment, the feedstock comprises oleic acid as the unsaturated fatty acid in an amount of at least 40% by weight. In an alternative embodiment, the feedstock comprises at least 70% by weight oleic acid.

15

Examples of zeolitic materials employable in the present embodiment include, but are not limited to zeolites having the following framework structures: AEL, AFO, AHT, BOG, CGF, CGS, CON, DFO, FAU, FER, HEU, AFS, AFY, BEA, BPH, CLO, EMT, FAU, GME, MOR, MFI, and the like.

20

Other catalytic materials having a three dimensional pore structure can be employed in this embodiment of the invention provided that they contain at least one channel structure having a pore size large enough for the fatty acid to enter the pore and access the internal active sites. Examples of such
25 materials include but are not limited to acidic clays and molecular sieves.

In another embodiment, the invention contemplates a process for the skeletal isomerization and hydrogenation of unsaturated linear fatty acids to saturated branched fatty acids in a single batch. This process comprises contacting said
30 unsaturated linear fatty acids with at least one acidic support material loaded with at least one metal capable of hydrogenating unsaturated chemical bonds in the presence of hydrogen or a hydrogen source. In this embodiment, the acidic

support material provides the acidic sites for the isomerization of unsaturated fatty acids and the metals allow for subsequent hydrogenation of the branched unsaturated fatty acids to saturated ones. A main advantage of this process is that the isomerization and the hydrogenation can be performed on a single catalyst and in a single batch.

In another embodiment, the skeletal isomerization and hydrogenation is conducted by a mixture of two or more catalysts, i.e., at least one acidic catalyst providing the requisite acidic sites for the isomerization of the unsaturated fatty acids and at least one catalyst loaded with at least one metal capable of hydrogenating the branched unsaturated fatty acids to saturated ones. In this embodiment, the isomerization and hydrogenation is performed in two steps in a single batch, i.e., for example, in a fixed bed reactor.

Examples of acidic support materials having utility in this embodiment of the invention include but are not limited to acidic zeolites and acidic clays and the like.

Zeolites usefully employed in this embodiment of the invention are typically acidic zeolites with or without metal ions, in addition to protons. Specific examples of zeolite structures include, but are not limited to faujasite, mordenite, USY, MFI, Mor, Y and Beta types.

Useful catalysts also include acidic clays with or without metal ions.

It is to be understood that if said acidic zeolites and/or said acidic clays are not loaded with metal ions, then a separate catalyst loaded with at least one metal capable of hydrogenating the branched unsaturated fatty acids may optionally be employed.

Whether a single catalyst is employed or whether two or more catalysts are employed, metal loading is typically below 20%.

Examples of suitable metals include, but are not limited to, Pt, Pd, Rh, Ir, Ru, Ni, Co, Cu and the like.

- 5 The invention will be illustrated by the following nonlimiting examples.

Example 1-3

These three examples show the conversion of oleic acid and the yield of
10 branched fatty acid at different reaction periods on H-Beta zeolite catalysts.
Experiments were carried out in a 135 ml autoclave reactor. For each reaction,
two grams of H-Beta catalyst (Si/Al=25, pellets with 1 mm in diameter and 1-2
mm in length, precalcined in air at 550°C) and 20 grams of oleic acid were
loaded into the reactor under nitrogen. Under agitation, the reactor was heated
15 to 250°C within 30 minutes and maintained at this temperature for a specified
time period (3 h in Example 1, 5 h in Example 2, and 7 h in Example 3,
respectively). The reaction was terminated by cooling to room temperature within
20 minutes. The mixture was brought out of the reactor and the liquid product
was separated from the solid catalyst by filtration. Compositions of feed and
20 reaction products were shown in Table 1.

Results in Table 1 show that the conversion of oleic acid increased with the
increase of reaction time. In the case of C₁₈ unsaturated fatty acid (C₁₈¹) in
Example 3, the conversion is 68 wt% and the selectivity to its branched isomers
25 is 79.5 wt%.

Example 4

Two grams of H-Beta catalyst (Si/Al=50, powder, calcined in air at 550°C) and 20
30 grams of oleic acid were loaded into the reactor under nitrogen. Under agitation,
the reactor was heated to 250°C within 30 minutes and maintained at this
temperature for 7 h. The reaction was terminated by cooling to room temperature
within 20 minutes. The mixture was taken out of the reactor and the liquid

product was separated from the solid catalyst by filtration. Reaction results were shown in Table 1.

The conversion of C₁₈¹ fatty acid is 74.1 wt% and the isomerization selectivity is
5 79 wt%.

Example 5

Two grams HY catalyst (Si/Al=80, powder, calcined in air 550°C) and 20 grams
10 of oleic acid were loaded into the reactor under nitrogen. Under agitation, the reactor was heated to 250°C within 30 minutes and maintained for 5 h. The reaction was terminated by cooling to room temperature within 20 minutes. The mixture was taken out of the reactor and the liquid product was separated from the solid catalyst by filtration. Reaction results were shown in Table 1.

15

Table 1

	Time (h)	<=C ₁₀	i-C ₁₂	C ₁₂	i-C ₁₄	C ₁₄ ¹	C ₁₄	i-C ₁₆	C ₁₆ ¹	C ₁₆	i-C ₁₈	C ₁₈ ¹	C ₁₈	lacton
Feed	-	0.1	0.3	0.3	0.1	0.5	2	1.4	4.8	4.0	2.1	74.6	4.3	5.5
Example 1	3	0	0.1	0.1	0.1	0	2.0	2.0	2.6	4.9	20.4	47.6	6.2	14.0
Example 2	5	0.1	0.2	0.4	0.2	0	2.2	2.2	2.1	5.3	26.1	40.7	4.0	16.5
Example 3	7	0.1	0.4	0.2	0.2	0	2.5	3.3	1.2	5.9	42.4	23.9	6.0	13.9
Example 4	7	0.1	0.4	0.4	0.1	0	2.8	3.8	1.2	6.4	45.8	19.3	5.9	13.8
Example 5	5	0.1	0.2	0.1	0	0	2.2	2.0	2.9	5.5	18.3	46.5	8.1	14.1

C₁₈¹ = C18:1 ; i-C₁₈ = isomerized C18 ; C₁₈ = saturated fatty acid already present in the feed ; similar for C12, C14, and C16 compounds.

20

Example 6

Two grams of H-Beta catalyst (Si/Al=50, powder, precalcined in air at 550°C) and 20 grams of erucic acid were loaded into the reactor under nitrogen. Under agitation, the reactor was heated to 250°C within 30 minutes and maintained for 5 h. The reaction was terminated by cooling to room temperature within 20 minutes. The mixture was taken out of the reactor and the product was separated from the solid catalyst by filtration with slightly heating. Compositions of erucic acid and reaction product were shown in Table 2.

10

These results indicated that erucic acid was highly branched.

Example 7

15 Two grams H-Beta catalyst (Si/Al=25, pellets with 1 mm in diameter and 1-2 mm in length, precalcined in air at 550°C) and 20 grams of erucic acid were loaded into the reactor under nitrogen. Under agitation, the reactor was heated to 280°C within 30 minutes and maintained for 5 h. The reaction was terminated by cooling to room temperature within 20 minutes, the mixture was taken out of the 20 reactor and the liquid product was separated from the solid catalyst by filtration. Compositions of erucic acid and reaction product were shown in Table 2.

Table 2

	C ₂₀	i-C ₂₂	C ₂₂ ¹	C ₂₂	i-C ₂₄	C ₂₄	Other
or less							
Feed	4.7	0.3	88.5	2.1	0	3.8	0.5
Example 7	4.7	69.2	11.5	5.7	3.7	0	5.2
Example 8	4.7	70.8	11.4	5.6	4.2	0	3.3

25

Example 7 showed that a similar isomerization result as that in Example 6 was achieved at a higher temperature but at a shorter reaction time.

Example 8

Two grams of H-Beta catalyst (Si/Al=50, powder, precalcined in air at 550°C) was loaded into a glass fixed bed reactor. A thermocouple in a thermowell was placed in the center of the catalyst bed. The catalyst was activated at 350°C for 3 h in a 20 ml/min nitrogen flow. After activation, the reactor temperature was lowered to 250°C and nitrogen flow rate was decreased to 1 ml/min. Oleic acid was pumped into the reactor at 2 ml/h. The results are shown in table 3, which indicate that a fixed bed process is also viable for the skeletal isomerization of unsaturated linear alkylcarboxylic acids.

Table 3

	Time (h)	<=C ₁₀	i-C ₁₂	C ₁₂	i-C ₁₄	C ₁₄ ¹	C ₁₄	i-C ₁₆	C ₁₆ ¹	C ₁₆	i-C ₁₈	C ₁₈ ¹	C ₁₈	lacton
Feed	-	0.1	0.3	0.3	0.1	0.5	2	1.4	4.8	4.0	2.1	74.6	4.3	5.5
Sample 1	2	0	0.9	0	0	0	3.0	6.3	2.0	8.7	38.9	21.8	6.0	12.4
Sample 2	4	0	0.4	0	0	0	1.9	0.3	3.4	5.2	25.8	35.8	3.9	23.3
Sample 3	6	0	0.2	0	0	0	1.8	1.6	2.6	4.9	19.4	47.9	3.5	18.1

Example 9

Two grams of Eu³⁺ exchanged Beta zeolite catalyst (Si/Al=50, powder, precalcined in air at 550°C) and 20 grams of oleic acid were loaded into the reactor under nitrogen. Under agitation, the reactor was heated to 250°C within 30 minutes and maintained for 7 h. The reaction was then terminated by cooling to room temperature within 20 minutes. The mixture was taken out of the reactor. The product was a liquid at room temperature and was separated from catalyst by filtration. GC analysis showed about 46% branched oleic acid yield from oleic acid (C₁₈¹).

Comparative Example 1

Zeolite with one dimensional channel /pore structure

Two grams Na-Mordenite catalyst (Zeolyst CP 500C-11, Si/Al=10, powder, precalcined in air at 550°C) and 20 grams of oleic acid were loaded into the reactor under nitrogen. Under agitation, the reactor was heated to 250°C within 30 minutes and maintained for 7 h. The reaction was then terminated by cooling to room temperature within 20 minutes. The mixture was taken out of the reactor and the liquid product was separated from the solid catalyst by filtration. GC analysis showed that there was less than 10 wt% branched oleic acid formed.

Comparative Example 2

Two grams H-Mordenite catalyst (obtained by precalcination of NH₄⁺ exchanged mordenite from Zeolyst CP 500C-11 at 550°C) and 20 grams of oleic acid were loaded into the reactor under nitrogen. Under agitation, the reactor was heated to 250°C within 30 minutes and maintained for 5 h. The reaction was then terminated by cooling to room temperature within 20 minutes. The mixture was taken out of the reactor. The product was solid at room temperature and it was separated from solid catalyst by melting and filtration. GC analysis showed that there was less than 10 wt% branched oleic acid formed.

Example 10

Pt-HBeta, Isomerization only

Ion exchange was carried out on a NH₄⁺ Beta zeolite (Si/Al=50) using tetraammineplatinum nitrate solution. The exchanged catalyst was calcined in air at 550°C before use. Two grams of this catalyst (Pt-HBeta) and 20 grams of oleic acid were loaded into the reactor under nitrogen. After sealed, the reactor was purged three times with ultra high purity nitrogen. A nitrogen pressure of 13.8 barg was approached at room temperature. With stirring at 1000 RPM, the mixture of oleic acid and catalyst was heated to 250°C within 30 minutes and

maintained for 7 h. After cooled down to room temperature within 20 minutes, the mixture was brought out of the reactor and the liquid product was obtained for analysis after separated from the solid catalyst by filtration. Compositions of feed and reaction products were shown in Table 4.

5

Example 11

Pt-HBeta, Isomerization (250°C, 7 hr) followed by hydrogenation;
Two grams of Pt-HBeta catalyst and 20 grams of oleic acid were loaded into the
10 reactor under nitrogen. After sealed, the reactor was purged three times with
ultra high purity nitrogen. A nitrogen pressure of 13.8 barg was approached at
room temperature. With stirring at 1000 RPM, the mixture of oleic acid and
catalyst was heated up to 250°C within 30 minutes and maintained for 7 h. The
pressure was about 24.1 barg under these conditions. Hydrogen was added to
15 reach a total pressure of 58.6 barg. Reaction was continued for another 2 h.
After cooled down to room temperature within 20 minutes, the solid mixture was
brought out of the reactor. The reaction product was obtained for analysis after
separated from the solid catalyst by filtration with slightly heating. Product
composition was shown in Table 4.

20

Table 4

Example	<=C ₁ o	i-C ₁₂	C ₁₂	i-C ₁₄	C ₁₄ '	C ₁₄	i-C ₁₆	C ₁₆ '	C ₁₆	i-C ₁₈	C ₁₈ '	C ₁₈	lacton
feed	0.09	0.26	0.32	0.11	0.46	2	1.37	4.83	4.01	2.07	74.57	4.29	5.62
1	0	0.39	0.11	0.36	0	2.79	3.01	1.05	6.6	43.03	18.94	4.14	19.58
2	0.04	0.6	0.1	0.89	0	2.46	4.71	0.31	7.44	49.21	1.86	27.59	4.79

25

Example 12

Pt-HBeta, Isomerization (250°C, 15 h) followed by hydrogenation; Three grams of Pt-HBeta catalyst and 30 grams of oleic acid were loaded into the reactor under nitrogen. After sealed, the reactor was purged three times with ultra high purity nitrogen. A nitrogen pressure of 3.5 barg was approached at 5 room temperature. With stirring at 1000 RPM, the mixture of oleic acid and catalyst was heated up to 250°C within 30 minutes and maintained to the end of the run. The pressure was about 9.0 barg under these conditions. A sample (sample 1) was taken at 14 h. After 15 h, hydrogen was added to reach a total pressure of 41.4 barg. Reaction was continued for another 6 h. After cooled 10 down to room temperature within 20 minutes, the mixture was brought out of the reactor. The reaction product (Sample 2) was obtained for analysis after separated from the solid catalyst by filtration. Product Composition was shown in Table 5.

15 Table 5

Sample	<=C ₁	i-C ₁₂	C ₁₂	i-C ₁₄	C ₁₄ ¹	C ₁₄	i-C ₁₆	C ₁₆ ¹	C ₁₆	i-C ₁₈	C ₁₈ ¹	C ₁₈	Lacton
1	0.45	1.22	0	0.56	0	2.56	2.97	0.78	7.5	56.38	9.43	8.87	9.28
2	0.58	1.83	0	1.18	0	3.13	7.08	0.68	8.64	57.2	1.03	17.83	0.82

The conversions of C₁₈ unsaturated fatty acid in the three samples above and the selectivities to branched fatty acids were shown in Table 6. About 10 wt% of 20 C₁₈ fatty acid was hydrocracked in sample 2.

Table 6

Sample	C ₁₈ ¹ conversion (wt%)	Isomerization selectivity (wt%)
1	87.35	83.37 (Unsaturated)
2	98.62	74.97 (Saturated)

Example 13

Pt-HBeta, Isomerization (280°C, 5h) followed by hydrogenation;

Two grams of Pt-HBeta catalyst and 20 grams of oleic acid were loaded into the reactor under nitrogen. After sealed, the reactor was purged three times with ultra high purity nitrogen. A nitrogen pressure of 3.5 barg was approached at room temperature. With stirring at 1000 RPM, the mixture of oleic acid and catalyst was heated up to 280°C within 30 minutes and maintained for 5 h. After cooled down to 200°C, the nitrogen was replaced with barg hydrogen and reaction was continued for another 4 h. The mixture was brought out of the reactor and the liquid product was obtained for analysis after separated from the solid catalyst by filtration. Composition of the reaction product was shown in Table 7.

Table 7

Example	<=C ₁₀	i-C ₁₂	C ₁₂	i-C ₁₄	C ₁₄ '	C ₁₄	i-C ₁₆	C ₁₆ '	C ₁₆	i-C ₁₈	C ₁₈ '	C ₁₈	lacton
4	0.59	1.79	0.25	2.4	0	3.9	11	1.9	10.8	53.21	2.21	8.04	4.02

Example 14

Pd-HBeta, Isomerization (280°C, 5 h) followed by hydrogenation;

Ion exchange was carried out on NH₄⁺ Beta zeolite (Si/Al=50) using tetraamminepalladium nitrate solution. The exchanged catalyst was calcined in air at 550°C and reduced with hydrogen (20 ml/min) in a fixed bed reactor at 250°C for 2h before use. Two grams of reduced Pd-HBeta catalyst and 20 grams of oleic acid were loaded into the reactor under nitrogen. After sealed, the reactor was purged three times with ultra high purity nitrogen. A nitrogen pressure of 3.5 barg was approached at room temperature after a leak test at 41.4 barg N₂ showed a good sealing. With stirring at 1000 RPM, the mixture of oleic acid and catalyst was heated up to 280°C within 30 minutes and maintained for 5 h. After cooled down to 200 °C, the nitrogen was replaced with 37.9 barg hydrogen and reaction was continued for another 4 h. The mixture was

brought out of the reactor and the product was obtained for analysis after separated from the solid catalyst by filtration. Composition of the reaction product is shown in Table 8.

5 Example 15

Pd-HBeta, Isomerization (250°C, 5 hr) followed by hydrogenation;

Two grams of Pd-HBeta catalyst (no hydrogen reduction) and 20 grams of oleic acid were loaded into the reactor under nitrogen. After sealed, the reactor was
 10 purged three times with ultra high purity nitrogen. A nitrogen pressure of barg was approached at room temperature after a leak test at 41.4 barg N₂ showed a good sealing. With an active stirring at 1000 RPM, the mixture of oleic acid and catalyst was heated up to 250°C within 30 minutes and maintained for 5 h. Then the nitrogen was replaced with 34.5 barg hydrogen and reaction was continued
 15 for another 2 h. The mixture was brought out of the reactor and the product was obtained for analysis after separated from the solid catalyst by filtration. Composition of the reaction product was shown in Table 8.

It shows that metallic palladium with hydrogenation function existed on the
 20 catalyst, therefore, no prereduction with hydrogen is necessary. The conversion of C₁₈ unsaturated fatty acid was 95.63 wt% with a selectivity to branched fatty acids of 67.83 wt%. There was no oligomerization or hydrocracked products.

Table 8

25

Example	<=C ₁₀	i-C ₁₂	C ₁₂	i-C ₁₄	C ₁₄ '	C ₁₄	i-C ₁₆	C ₁₆ '	C ₁₆	i-C ₁₈	C ₁₈ '	C ₁₈	lacton
5	0.58	2.05	0	1.7	0	3.5	9	0	9.88	56.54	2.19	14.4	0.24
6	0	0.32	0.1	0.7	0	2.5	3.9	0	7.46	50.44	3.26	24.11	7.18

Example 16

Pt-HY

Ion exchange was carried out on NH_4^+ Y zeolite (Si/Al=12) using 5 tetraammineplatinum nitrate solution. The exchanged catalyst was calcined in air at 550 °C before use. Two grams of this catalyst (Pt-HY) and 20 grams of oleic acid were loaded into the reactor under nitrogen. After sealed, the reactor was purged three times with ultra high purity nitrogen. A nitrogen pressure of 3.5 barg was approached at room temperature after a leak test at 41.4 barg N_2 showed a 10 good sealing. With stirring at 1000 RPM, the mixture of oleic acid and catalyst was heated up to 280 °C within 30 minutes and maintained for 5 h. After cooled down to 200 °C, the nitrogen was replaced with 34.5 barg hydrogen and reaction was continued for another 3 h. After cooled down to room temperature within 20 minutes, the mixture was brought out of the reactor and the product was 15 obtained for analysis after separated from the solid catalyst by filtration with slightly heating. Composition of the reaction product was shown in Table 9.

The conversion of C_{18} unsaturated fatty acid was 89.63 wt% with a selectivity to branched fatty acids of 47.16 wt%.

20

Example 17

Pt-HMor

Ion exchange was carried out on NH_4^+ Mordenite zeolite (Si/Al=20) using 25 tetraammineplatinum nitrate solution. The exchanged catalyst was calcined in air at 550 °C before use. Two grams of this catalyst (Pt-HMor) and 20 grams of oleic acid were loaded into the reactor under nitrogen. After sealed, the reactor was purged three times with ultra high purity nitrogen. A nitrogen pressure of 13.8 barg was approached at room temperature after a leak test at 41.4 barg N_2 showed a 30 good sealing. With stirring at 1000 RPM, the mixture of oleic acid and catalyst was heated up to 280°C within 30 minutes and maintained for 5 h. After cooled down to 200 °C, the nitrogen was replaced with 34.5 barg hydrogen and

reaction was continued for another 4 h. After cooled down to room temperature within 20 minutes, the mixture was brought out of the reactor and the product was obtained for analysis after separated from the solid catalyst by filtration with slightly heating. Composition of the reaction product was shown in Table 9.

5

Table 9

Example no	<=C	i-C ₁₂	C ₁₂	i-C ₁₄	C ₁₄ '	C ₁₄	i-C ₁₆	C ₁₆ '	C ₁₆	i-C ₁₈	C ₁₈ '	C ₁₈	lacton
7	0	0	0	1.59	0	1.41	0.23	0	12.26	33.59	7.73	37.71	5.48
8	0.84	2.1	0.33	2.43	0	4.03	14.3	0.62	11.45	50.14	0.74	9.25	3.77

CLAIMS

1. A process for the isomerization of a feedstock which comprises unsaturated linear fatty acids, alkyl esters of unsaturated fatty acids or mixtures thereof,
5 wherein said process comprises subjecting said feedstock to an isomerization reaction in the presence of an acidic catalyst having a three-dimensional channel pore structure wherein at least one channel structure has a pore size diameter of at least 6 Å.
- 10 2. The process of claim 1, wherein the isomerization of said feedstock comprises branching of the fatty acids or alkyl esters thereof.
- 15 3. The process of claim 1 wherein said acidic catalyst comprises a zeolite, acidic clay, molecular sieve, or mixtures thereof.
4. The process of claim 3 wherein said acidic catalyst comprises a zeolite
- 20 5. The process of claim 4 wherein said zeolite comprises at least one of the following framework structures: AEL, AFO, AHT, BOG, CGF, CGS, CON, DFO, FAU, FER, HEU, AFS, AFY, BEA, BPH, CLO, EMT, FAU, GME, MOR, MFI, or mixtures thereof.
- 25 6. The process of claim 4 wherein the SiO₂ /Al₂O₃ ratio of the zeolite is at least 10.
7. The process of claim 4 wherein said zeolite contains at least one channel structure having a pore diameter of at least 6.5 Å.
- 30 8. The process of claim 7 wherein said zeolite contains at least one channel structure having a pore diameter of at least 7 Å.

9. The process according to any one of the preceding claims wherein the feedstock comprises of at least 50% by weight of unsaturated fatty acids, alkyl esters of unsaturated fatty acids or mixtures thereof.
- 5 10. The process of claim 9 wherein the feedstock comprises of at least 70% by weight oleic acid.
11. The process of claim 9 or 10 wherein at least part of the isomerization is performed at a temperature of between 100° C and 350° C.
- 10 12. The process of claim 11 wherein at least part of the isomerization is carried out at a temperature of between 230°C and 285°C.
13. The process according to any one of the preceding claims wherein said isomerization is conducted in a batch reactor.
- 15 14. The process according to any one of the preceding claims wherein said isomerization is conducted in a fixed bed continuous flow reactor.
- 20 15. The process of claim 13 wherein the feedstock is contacted with the catalyst for a period of at least 30 minutes.
16. The process of claim 13 wherein the amount of catalyst used is between 0.5 and 20% by weight of the feedstock in the batch reactor.
- 25 17. The process of claim 13 wherein the amount of catalyst used is between 0.5 and 20% by weight of the space velocity of the feedstock in a continuous flow reactor.
- 30 18. The process of claim 4 wherein said zeolite having a three-dimensional pore structure comprises at least one pore structure containing 10-membered rings as catalysts.

19. The process of claim 4 wherein said zeolite having a three-dimensional pore structure comprises at least one pore structure containing 12-membered rings as catalysts.

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20. The process of claim 4 wherein said zeolite having a three-dimensional pore structure comprises at least one pore structure containing at least one ring having greater than 12 members as catalysts.

10 21. A process for the isomerization of a feedstock which comprises unsaturated linear fatty acids, alkyl esters of unsaturated fatty acids or mixtures thereof, wherein said process comprises subjecting said feedstock to an isomerization reaction in the presence of an acidic zeolite catalyst having a three-dimensional channel structure wherein at least one channel structure comprises rings having 15 at least 12 members as catalysts.

22. A process for the isomerization and hydrogenation of a feedstock which comprises unsaturated linear fatty acids, alkyl esters of unsaturated fatty acids or mixtures thereof, wherein said process comprises subjecting said feedstock to 20 isomerization and hydrogenation reactions in the presence of an acidic support material loaded with at least one metal capable of hydrogenating unsaturated chemical bonds in the presence of hydrogen or a hydrogen source.

23. The process of claim 22 wherein said acidic support material comprises 25 acidic clay, acidic zeolite, molecular sieve, or mixtures thereof.

24. The process of claim 22 wherein said acidic support material comprises acidic zeolite.

30 25. The process of claim 24 wherein said zeolite comprises a three-dimensional channel pore structure.

26. The process of claim 24 wherein said zeolite comprises at least one channel structure having a pore diameter of at least 6.0 Å.
27. The process of claim 24 wherein said zeolite having a three-dimensional pore structure comprises at least one pore structure comprised of rings having at least 12 members as catalysts.
5
28. The process of claim 24 wherein said acidic zeolite comprises at least one zeolite having one of the following frameworks: FAU, MFI, MOR, BEA.
10
29. The process of claim 24 wherein said metal comprises Pt, Pd, Rh, Ir, Ni, Co, Ru, Cu, or mixtures thereof.
30. The process claim 22 wherein at least part of the isomerization is performed
15 at a temperature of between 100° C and 350° C.
31. The process of claim 22 wherein said isomerization and hydrogenation is conducted in a batch reactor.
20
32. The process of claim 22 wherein said isomerization and hydrogenation is conducted in a fixed bed continuous flow reactor.
33. The process of claim 31 wherein the feedstock is contacted with the catalyst
25 for a period of at least 30 minutes.
34. The process of claim 31 wherein the amount of catalyst used is between 0.5 and 20% by weight of the feedstock in the batch reactor.
35. The process of claim 32 wherein the amount of catalyst used is between 0.5
30 and 20% by weight of the space velocity of the feedstock in a continuous flow reactor.

36. A process for the isomerization and hydrogenation of a feedstock which comprises unsaturated linear fatty acids, alkyl esters of unsaturated fatty acids or mixtures thereof, wherein said process comprises subjecting said feedstock to isomerization and hydrogenation reactions in the presence of a mixture of at least two types of catalysts, wherein at least one catalyst is an acidic catalyst material capable of isomerizing straight chain fatty acids or alkyl esters thereof into branched isomers, and at least one catalyst is a metal catalyst loaded with at least one metal capable of hydrogenating unsaturated chemical bonds in the presence of hydrogen or a hydrogen source, wherein said isomerization and hydrogenation is conducted in a single batch.
37. The process of claim 36 wherein said acidic catalyst material comprises acidic clay, acidic zeolite, acidic molecular sieve, or mixtures thereof.
38. The process of claim 36 wherein said acidic support material comprises acidic zeolite.
39. The process of claim 36 wherein said acidic zeolite comprises at least one zeolite having one of the following frameworks: FAU, MFI, MOR, BEA.
40. The process of claim 36 wherein said metal comprises Pt, Pd, Rh, Ir, Ni, Co, Ru, Cu, or mixtures thereof.
41. The process of claim 36 wherein at least part of the isomerization is performed at a temperature of between 100° C and 350° C.
42. The process of claim 36 wherein the feedstock is contacted with the catalyst for a period of at least 30 minutes.
43. The process of claim 36 wherein the amount of catalyst used is between 0.5 and 20% by weight of the feedstock in a batch reactor.

44. The process of claim 36 wherein said metal catalyst is a metal zeolite.

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(54) Title: SKELETAL ISOMERIZATION OF FATTY ACIDS

(57) Abstract: The present invention relates to a process for the skeletal isomerization of unsaturated linear fatty acids to branched fatty acids which comprises contacting said unsaturated linear fatty acids with at least one large pore zeolite catalyst wherein said at least one zeolite catalyst comprises a material having a three dimensional channel structure having a pore diameter of at least 6.0 Å. In another embodiment, the invention relates to a process for the skeletal isomerization and hydrogenation of unsaturated linear fatty acids to saturated branched fatty acids which comprises contacting said unsaturated linear fatty acids with at least one metal-zeolite catalyst.

INTERNATIONAL SEARCH REPORT

Int'l	Application No
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A. CLASSIFICATION OF SUBJECT MATTER							
IPC 7 B01J29/06 C07C51/353 C07C67/333 C07C57/02 C07C69/24 C07C53/126							
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C. DOCUMENTS CONSIDERED TO BE RELEVANT							
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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